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in Alkaline Pulping**

D. Dimmel, S. Anderson, and P.I. Sklar

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A STUDY AIMED AT UNDERSTANDING THE AQ/POLYSULFIDE SYNERGISTIC EFFECT IN ALKALINE PULPING

Donald Dimmel, Sean Anderson, and Perla Izsak Sklar

Institute of Paper Science and Technology
500 10th Street NW, Atlanta, GA 30318, USA
donald.dimmel@ipst.edu

ABSTRACT

When polysulfide (PS) and anthraquinone (AQ) are employed together during alkaline pulping, the yield gain and the extent of delignification during pulping are more than expected based on simple additive effects. The reactions of two lignin model compounds were studied in an attempt to better understand the PS/AQ synergism chemistry. Diagnostic products were not observed with an “electron detector” compound; instead, it appears that PS preferentially oxidized the compound. Reactions of a “clock” compound indicated that PS could not reduce AQ to anthrahydroquinone (AHQ) at 140°C. However, the data indicated that β -aryl ether fragmentation efficiencies for PS were better than sodium sulfide, the lignin active reagent in kraft pulping. In addition, AQ was observed to fragment the clock model by non-quinone methide chemistry.

INTRODUCTION

A synergism exists when using polysulfide (PS) and anthraquinone (AQ) together in alkaline pulping; the pulp yield and extent of delignification are more than expected based on simple additive effects.¹ The reasons for this are not well understood and led us to conduct the studies outlined herein.

The chemistry associated with delignification and yield gains with each individual reagent is fairly well understood. Anthrahydroquinone (AHQ) causes lignin to fragment and dissolve by means of electron transfer chemistry.²⁻⁵ Some recent studies suggest that polysulfide might aid delignification by destroying lignin vinyl ether structures,⁶ normally a difficult unit to fragment during pulping.⁷ The carbohydrate stabilization reactions likely involve transferring two electrons from an enediol to an oxidizing agent, either in one step or two one-electron steps (Figure 1).⁸ The oxidizing agent could be either polysulfide or AQ.

PLACE FIGURE 1 HERE

Anthraquinone and its reduced form, AHQ, participate in redox reactions that lead to carbohydrate oxidation and lignin reduction (fragmentation), as shown in Figure 2.⁹ Typically, the redox cycle is shown to involve only AQ and AHQ dianion. However, this simple picture has a serious flaw: to become reduced and soluble in the pulping liquor, AQ needs to react with *soluble* carbohydrate materials. Such reactions are of *no value* with respect to gains in pulp yield. It is only when AQ reacts with insoluble carbohydrates, such as cellulose, that yield gain will be realized. However, because AQ has very limited solubility in 1M NaOH,¹⁰ one would expect little or no reaction with insoluble, polymeric carbohydrates. A way around this discrepancy is to *first* have soluble carbohydrates reduce AQ to anthrahydroquinone ion radical, a water-soluble material; the ion radical could then oxidize insoluble carbohydrates. In this scenario, the redox cycle would consist of a shuttling back and forth between the partially reduced AHQ ion radical and fully reduced AHQ dianion; thus, AQ is bypassed. There is a large body of evidence that supports a single electron transfer reaction occurring between AHQ dianion and lignin that would result in the production of AHQ ion radical and fragmented lignin.²⁻⁵

PLACE FIGURE 2 HERE

So, how could a mixture of polysulfide and AQ enhance yields and pulping rates? The answer might lie in the ability of PS to reduce either AQ or AHQ ion radical (Figure 3). If oxidation/reduction potentials are right, polysulfide, a *soluble* component, should reduce *insoluble* AQ much faster than *insoluble* carbohydrates. A two-electron reduction of AQ would produce high levels of AHQ⁻² that would assist lignin fragmentation. A one-electron reduction of AHQ ion radical would give the same result. The synergism between AQ and PS can be explained by this scheme if either elemental sulfur or polysulfide ion radical is more efficient at oxidizing carbohydrates than polysulfide dianion or AHQ ion radical. Since the oxidation (stabilization) involves electron transfer from the carbohydrate, we expect sulfur or PS ion radical would accept electrons better than PS dianion; it is more difficult to add charge to a species that is already extensively charged. Our research was aimed at establishing the validity of this hypothesis.

PLACE FIGURE 3 HERE

RESULTS

An easy test of whether polysulfide could reduce AQ to AHQ in NaOH solution is to just put the reagents together in an Erlenmeyer flask and heat to boiling, while bubbling nitrogen through the solution. With AQ/dithionite or AQ/glucose, you observe the production of the deep red AHQ dianion. A polysulfide solution, which is already orange before the addition of AQ, appeared to darken very little when heated in alkali. Thus, under these conditions, S_x^{-2} is not able to reduce AQ to AHQ^{-2} . The reaction requires that the oxidation potentials of polysulfide and AQ be close in value. Maybe this is not the case. However, such a reduction might be possible between S_x^{-2} and AHQ radical anion. Thus, the easy experiment did not provide the full answer, and other avenues were explored. We examined two approaches, both based on previous work in our laboratory.

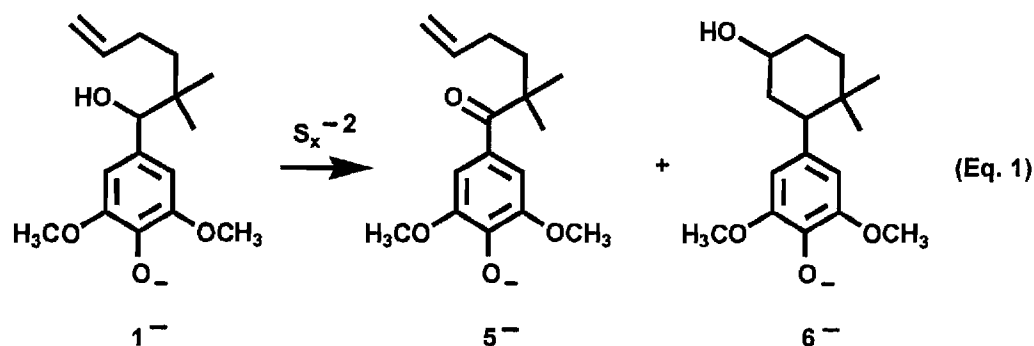
Reactions of the Electron Transfer Detector Compound

Our first approach involved studying the chemistry of **1**, a compound that we term the "electron transfer detector (ETD)" compound.^{3,11} In base at 135°C, it is converted to a quinone methide (QM **2**); reagents that can transfer electrons to the QM lead to the reduction products **3** and **4**, highlighted in Figure 4. Cyclization to a 5-membered ring (**4**) is evidence that radical intermediates were formed.

PLACE FIGURE 4 HERE

If less than one equivalent of AHQ is present, we expect incomplete reaction and less formation of reduced products. However, if polysulfide is present in excess amounts, the AHQ dianion might be regenerated. The reaction of 5 equivalents of polysulfide and 0.1 equivalent of AHQ may produce the high levels of reduced products that were observed when using 2 equiv. of AQ and 5 equiv. of glucose.³

When heated with polysulfide at 135°C, the ETD compound did not provide the expected products. Instead, we observed two principal products, which were tentatively assigned structures based on GC/MS evidence and on our general knowledge of MS fragmentation patterns of similar compounds.¹² One of the products was obviously the ketone **5**, an expected oxidation product. The spectrum displayed a molecular ion two units less than the ETD compound and exhibited a strong acylium ion ($ArC=O^+$) signal. The spectrum of the other product indicates it was an isomer of the ETD compound, suggesting the 6-membered ring cyclic structure **6**. Such a product would be indicative of a carbocation being generated at the benzylic carbon.



Based on this discouraging result with PS, we did not pursue further experiments with AQ/PS/ETD compound mixtures. Instead, we examined an alternative approach to studying possible PS/AQ electron transfer chemistry.

Reactions of the Clock Compound

The “clock” compound, β -aryl ether model **7**, has previously been used to determine the relative efficiencies of reagents to induce β -aryl cleavage reactions.¹³ Model **7** generates QM **8** at high temperature in alkali (Fig. 5, path *a*). The side chain terminal hydroxyl group, probably ionized at high pH, can internally react with the QM intermediate to give a cyclic product **9** (Fig. 5, path *b*). The rates of other QM reactions can be “clocked” relative to the cyclization event by determining the yields of different products in comparison to the yield of the cyclic product **9**. Besides cyclization, the model can react with pulping chemicals to give β -aryl ether cleavage (via path *c*, Fig. 5) or with base to give vinyl ether **10** (path *d*). A high proportion of scission versus cyclization signifies conditions corresponding to efficient delignification.

PLACE FIGURE 5 HERE

Very little cyclization occurs when 5 equiv. of AHQ is reacted with **7**.¹³ In NaOH alone, the major product is cyclic product **9**. A mixture of NaOH and NaSH (kraft conditions) gives roughly an equal mixture of fragmentation and cyclization. If only 2 equivalents of AHQ are used in the model **7** degradations, the efficiency of fragmentation falls off by ~50%. However, the efficiency can be restored to 100% by adding 50% methanol to the 2 equiv.-AHQ reaction. The addition of 50% methanol to soda or kraft reactions of **1** had no positive benefits. To summarize our previous model **7** studies, we have seen a large synergism for AHQ/methanol and small synergism in the case AHQ/Na₂SO₃.¹³ The system looked to be an attractive one in which to observe possible synergism between AQ and PS.

Preliminary reactions of model 7 with AHQ

We examined three ways to generate AHQ; each employed deoxygenated aqueous NaOH. The first way involved forming, isolating, and adding AHQ to a reaction vessel containing model 7.¹³ However, achieving anaerobic conditions during all these steps, with the crude glove box at our disposal, proved difficult.

Alkaline hydrolysis of AHQ-diacetate gives AHQ⁻²; however, the hydrolysis reaction is very slow because of the very low water solubility of the diacetate. Fearing that hydrolysis would be slower than quinone methide generation, we first heated AHQ-diacetate with aqueous NaOH for an hour at 150°C in a sealed pressure vessel under anaerobic conditions in the absence of 7. The reaction vessel was cooled, opened in a glove box in a nitrogen atmosphere, compound 7 added, resealed, and heated again.

The third way was to generate AHQ by reducing AQ with sodium dithionite in an aqueous NaOH solution containing 7. Appropriate controls demonstrated that dithionite did not interfere with model 7 reactions. We principally used this last method. The dithionite reduction consumes four equivalents of NaOH. All reactions were conducted with 45 equivalents of NaOH/equiv. of 7. For example, when 2 equiv. each of AQ and dithionite were used, 53 equiv. of NaOH were employed to give 45 equiv. of NaOH after the reduction reaction.

Unlike our previous study,¹³ the reaction solutions were not acidified prior to HPLC analysis and a different internal standard, vanillyl alcohol, was employed. Constituent elution times changed somewhat; our previous internal standard no longer had a unique elution time. The high sample pH of the injected sample is nullified by dilution during the HPLC processing. These small changes allowed us to see a styrene product not previously seen, which helped explain the chemistry of PS pulping; more will be said about this later.

A series of 140°C reactions of 7 with different levels of AHQ (AQ/dithionite) produced the data shown in Figure 6. There is no basic difference in the yields of 9 (fragmentation) and 11 (cyclization) when using 1 equiv. or no AHQ. However, as the AHQ relative concentration was increased, fragmentation took on greater importance; at 5 equiv. of AHQ, 11 was observed in only 0.2% yield. While we strived for anaerobic conditions, it appears that our deoxygenated water still contained ~1⁺ equiv. of O₂, enough to convert some AHQ back to AQ. Anthraquinone has much less effect on 7 in NaOH than AHQ; more will be said about this later. A preliminary 150°C run, involving different levels of AHQ-diacetate and NaOH, gave results similar to those shown in Figure 6.

PLACE FIGURE 6 HERE

As seen in Figure 6, when fragmentation is high, cyclization is low. However, there was not always a perfect correlation between the two. To get better accuracy, we focused on the cyclization product (9) yield, since its HPLC signal was always Gaussian; the guaiacol signal was not always Gaussian, suggesting the presence of an occasional interfering signal.

Reactions of 7 with Na₂S_x, NaSH, and combinations with AHQ

Since polysulfide decomposes at high temperatures in alkali,¹⁴ we conducted the PS/model 7 reactions at 140°C. Figure 7 highlights the results of several 140°C cooks of 7 with different reagents and combinations of reagents, all performed under anaerobic conditions for one hour. The low level of cyclization product 9 in the case of 2 equiv. of AQ and 5 equiv. of dithionite signifies highly efficient fragmentation. Both residual oxygen in the solution and reaction with QM 8 consume the initial AHQ⁻² in the solution; however, the excess available dithionite converts AQ (or AHQ ion radical) back to AHQ⁻², thereby effectively raising the concentration of AHQ⁻² to ~5 equiv. for reaction with QM 8. Note that 2AQ/2dithio/5PS and 2AQ/2dithio have about the same effectiveness, meaning that *PS is not reducing AHQ ion radical or AQ*.

PLACE FIGURE 7 HERE

Product distributions when reacting 7 at 140°C for different time periods with 2AQ/2dithio/5PS are shown in Figure 8. The purpose of doing a time study (several were done) is to verify reaction trends, rather than relying totally on the data of one time to draw conclusions. The trend observed in this case models what we have previously seen with only modestly effective fragmentation conditions.¹³ The cyclized compound can reverse back to the QM 8 and be lost with time.

PLACE FIGURE 8 HERE

Dithionite causes no increase in fragmentation of 7; this is apparent from the similar efficiencies of 5PS/2dithio to that of 5PS and of 5NaSH/2dithio to that of 5NaSH. It is also apparent that 2AQ/2dithio is better at fragmenting the model than 5NaSH, even considering that some of the AHQ is consumed by O₂-reactions. The fact that AHQ >> NaSH has been noted before.¹³ You might think that 5NaSH/2AQ/2dithio would be as good as, or even better than 2AQ/2dithio, since NaSH positively effects fragmentation. The data below appears to contradict this conclusion; however, it is likely than the degassed NaSH solution may have contained some dissolved oxygen that effectively hurt the level of AHQ⁻² in solution.

Comparison of model 7 fragmentation efficiencies for Na₂S_x and NaSH

The Figure 7 data suggest that PS may be a somewhat better reagent than NaSH in fragmenting model 7 at 140°C. Additional experiments were conducted to establish this fact. The product distribution when reacting 7 at 140°C for 1 hour with different levels of PS (Figure 9) indicates a good correlation of PS concentration and fragmentation efficiency. At 10 equiv. of PS the yield of guaiacol was 70% and cyclic compound <10%.

PLACE FIGURE 9 HERE

Table 1 gives data that compare the product distribution for reacting 7 for 1 hour at 140°C with either 5 equiv. of PS or NaSH. The data clearly demonstrate that polysulfide is more effective than sodium sulfide in fragmenting model 7.

Table 1. Product distribution for three 1-hour 140°C reactions of 7 with either 5 equiv. of PS or NaSH.

<u>Additive</u>	<u>% Cycl. Cpd. (9)</u>	<u>% 9 Av.</u>	<u>% Guaiacol (11)</u>	<u>% 11 Av.</u>
PS	27.8, 25.5, 25.0	25.8	46.8, 45.0, 44.1	45.3
NaSH	31.1, 32.4, 31.9	31.8	32.1, 32.9, 33.4	32.8

Model 7 reaction products

In general, the yields of 7, 9, and 11 totaled 80-100%. Reactions involving AHQ and PS displayed an HPLC signal that we assigned to styrene structure 12. Complete ultraviolet spectra for eluting HPLC signals were occasionally recorded. Compounds 7, 9, and 11 had similar UV spectra, while the styrene component 12 had a spectrum closely matching that of coniferyl alcohol.¹⁵ The fact that the levels of 11 and 12 were closely related (discussed later) argued for the structural assignment of 12. The only other major signals observed were fast eluting ones in the cases of NaSH and Na₂S_x cooks, which were assigned to UV-absorbing inorganic sulfur compounds; such signals were present in PS solutions containing no model. An example chromatograph is provided in the Experimental Section.

Other possible products include: polysulfide adduct 13 and ketone 14 (or its hemiacetal 15). The relatively high material balance and clean product distribution indicate that these components are probably not present. The UV evidence indicates that these are not coeluting with other components; it is unlikely that they have very long retention times (outside our 25-min HPLC run time).

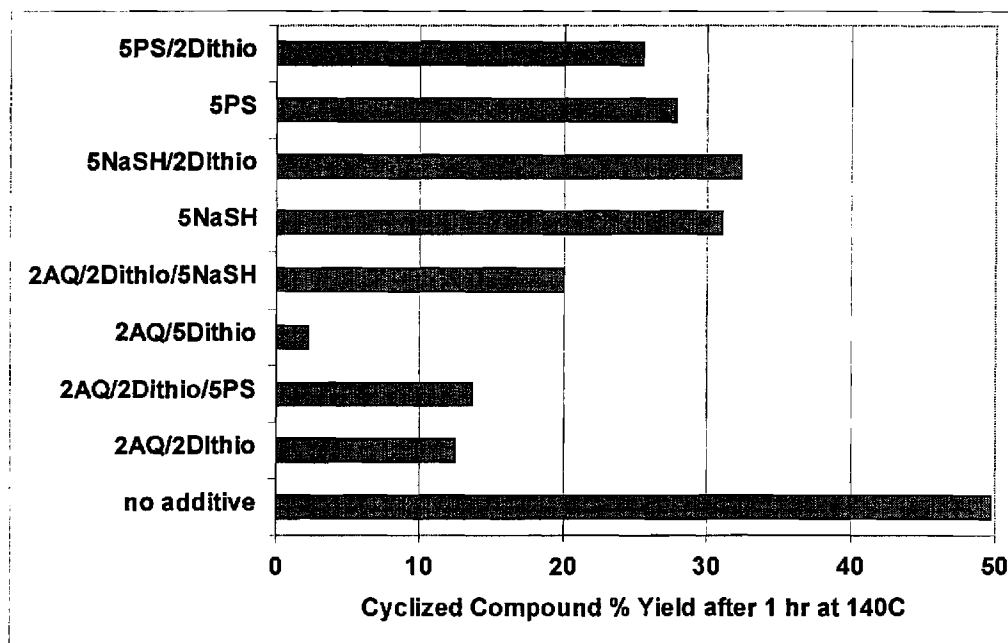


Figure 7. Amount of compound 11 formed when reacting 7 at 140°C for 1 hour with different reagent combinations.

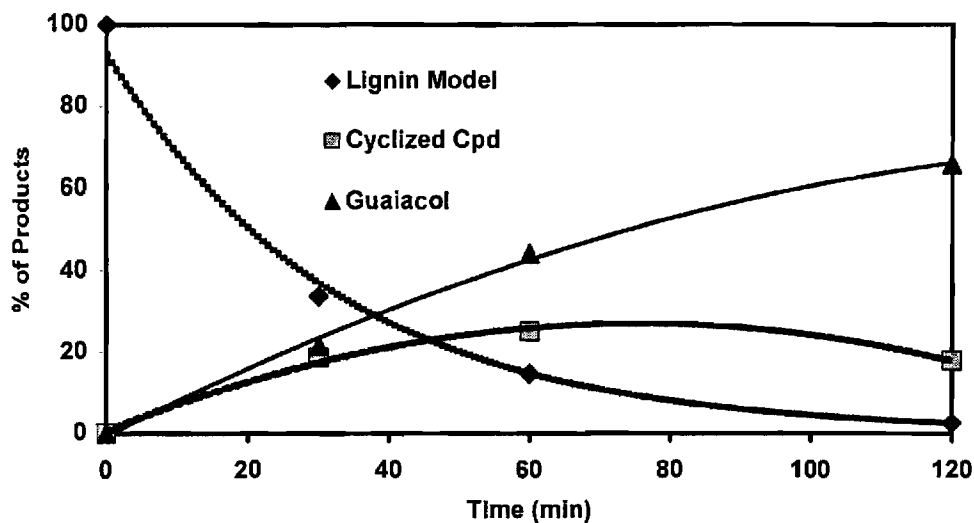


Figure 8. Product distribution when reacting 7 at 140°C for different time periods with 2AQ/2dithio/5PS.

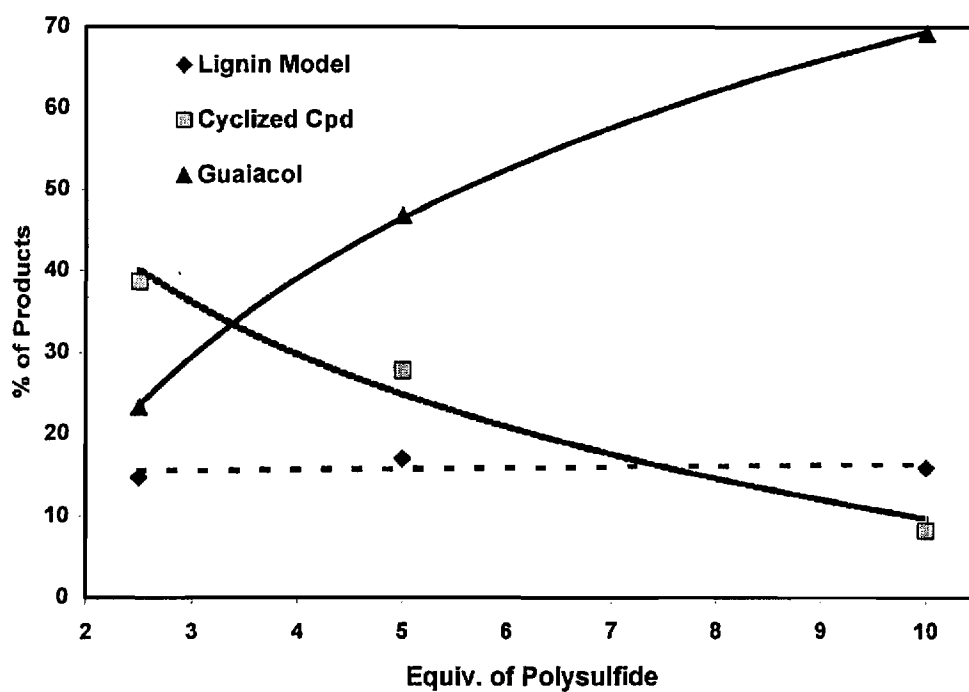


Figure 9. Product distribution when reacting 7 at 140°C for 1 hour with different levels of PS.

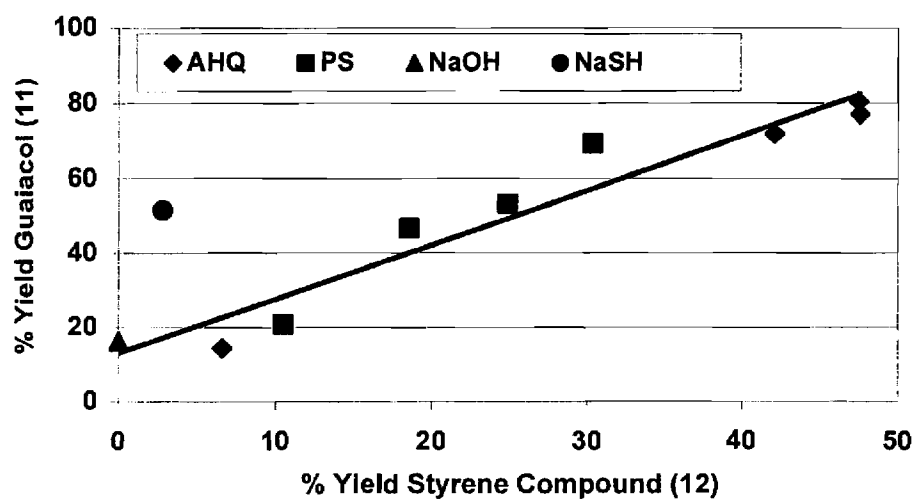


Figure 10. Correlation of the levels of styrene 12 and guaiacol (11) when treating model 7 at 140°C for 1 hour with different additives.

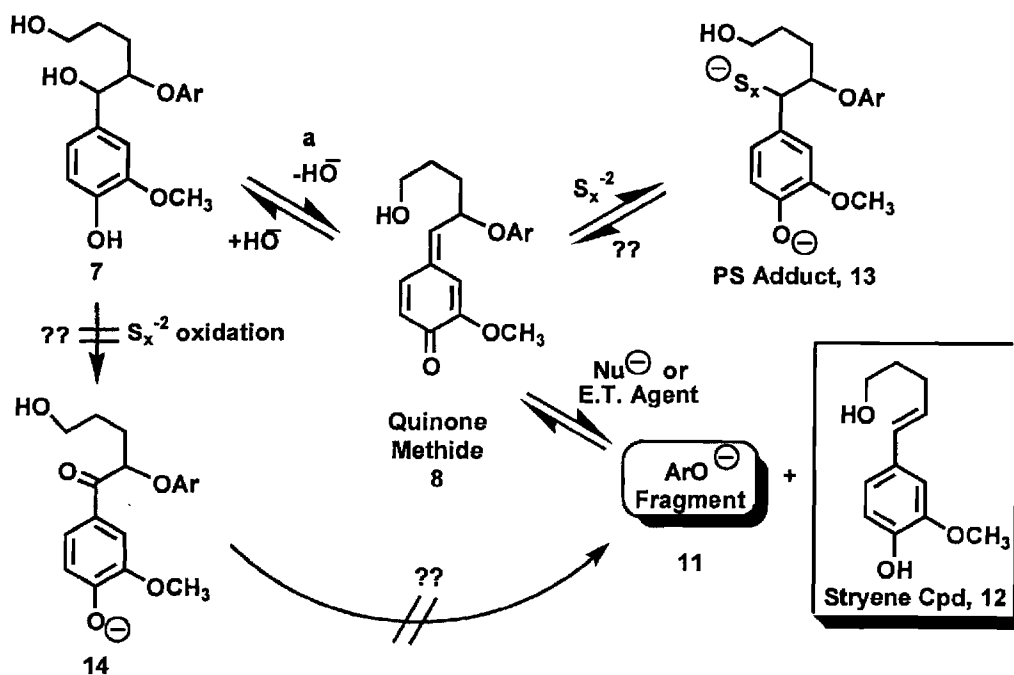


Figure 11. Proposed reactions of model 7 in the presence of polysulfide.

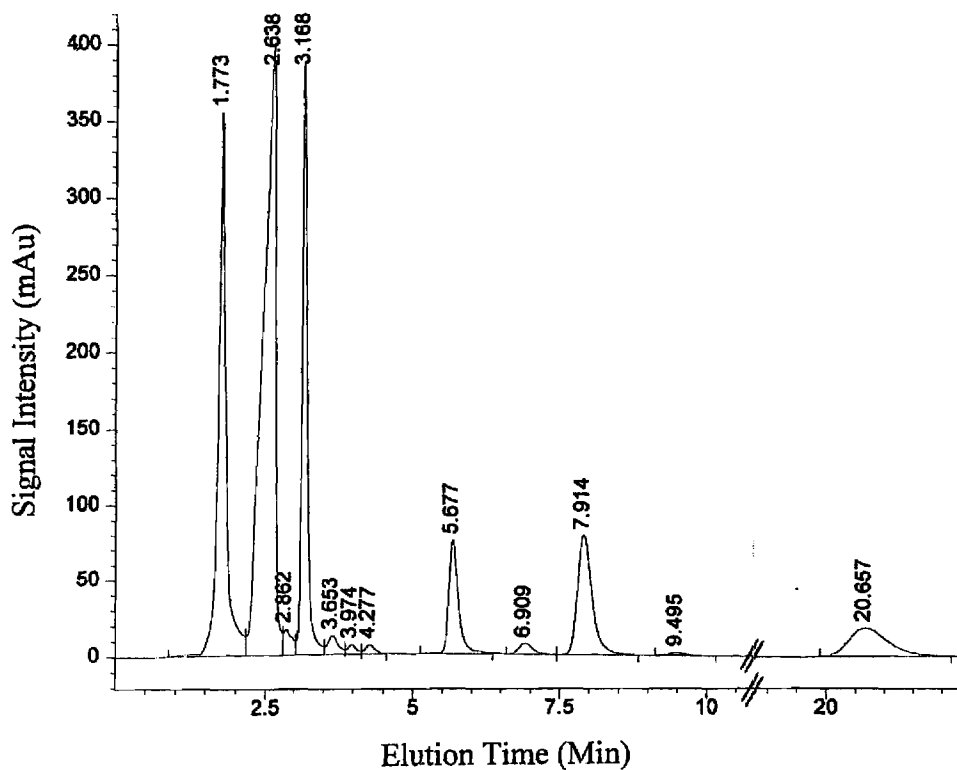


Figure 12. HPLC chromatogram of the product mixture of a 2-hr 140°C reaction of model 7 with 2AQ/2dithio/5PS.